

Catalytic metal free production of large cage structure carbon particles: A candidate for hydrogen storage

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We will demonstrate that carbon particles consisting of large cages can be produced without catalytic metal. The carbon particles were produced in CO gas as well as by introduction of 5 % methane gas into the CO gas. The as-produced carbon particles were able to absorb approximately 16.2 wt% of hydrogen. This value is 2.5 times higher than the 6.5 wt% goal for the vehicular hydrogen storage proposed by the Department of Energy in the USA. Therefore, we believe that this carbon particle is an excellent candidate for hydrogen storage for fuel cells.

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Hydrogen is one of the most promising fuel alternatives to petroleum and has the advantage that it produces clean energy for the environment. Because hydrogen is inexhaustible in contrast to finite petroleum reserves, and because it produces only water, i.e., no gases such as CO₂ or NO_x, concerns of global warming never arise. Although many advanced techniques have been discovered for hydrogen utilization, all of the requirements have not been achieved. Targets such as total cost, safety and storage efficiency depend on the size and weight of the storage medium. For example, in the case of liquid hydrogen, very low temperatures, ~20 K, are required, and it is unlikely those can be achieved for use on vehicles. In the case of compressed hydrogen gas, the density is too low for practical use. On the other hand, alloy materials such as LaNi₅, FeTi, Mg₂Ni and ZrV₂ cannot satisfy the storage requirement because they are too heavy. Recently, carbon nanotubes have attracted intense interest as hydrogen storage media.¹ Dillon and colleagues demonstrated the possibility for single-walled carbon nanotubes to yield ~5 to 10 wt% gravimetric storage density at room temperature. These values satisfied the goal of 6.5 wt%, decided by the Department of Energy in the USA for vehicular hydrogen storage. Subsequently, several kinds of experiments have been carried out.

A hydrogen uptake density of 8.25 wt% has been reported for crystalline ropes of single-walled carbon nanotubes (SWNT) at 80 K and 12 MPa.² Subsequently, Chen et al. (1999) reported that Li or K doped multi-walled carbon nanotubes adsorbed hydrogen to densities of 20 and 14 wt%, respectively.³ However, there has been some speculation that the high

uptake density was caused by the hydration of the alkaline metals.⁴ Liu and colleagues (1999) reported hydrogen adsorption of 4.2 wt% at room temperature and 10 MPa using SWNT with a mean diameter of approximately 1.85 nm.⁵ These types of SWNT have been produced using catalytic metals such as Fe, Co and Ni. The catalytic metals become contaminants during industrial utilization. In this paper, we will demonstrate the production of carbon particles with unique structure without catalytic metals, and their high uptake efficiency may make them useful components of hydrogen fuel cells.

Carbon smoke particles were prepared in the laboratory by vacuum evaporation using the Graphitic Smokes Apparatus. Smoke grains were produced at a total pressure of 200 Torr in a gas mixture of CO and He or CO and CH₄. A carbon electrode, with a thinned section at the middle, was prepared and vaporized via resistive heating. A thirty second run produced about 300 mg of black smoke. Ten samples of carbon smoke particles were produced with varying ratios of gases in the mixture.

Infrared spectra of the samples, embedded in KBr pellets, were measured with a Fourier-transform infrared spectrometer (Mattson Polaris FT-IR spectrometer). The infrared system utilized a KBr beam splitter and deuterated triglyceride sulfate detector. The wavelength resolution used for this work was 0.5 cm⁻¹.

The condensed smoke samples were mounted on holey amorphous carbon thin films supported by standard 200-mesh Cu Transmission electron microscope (TEM) grids. TEM observations were carried out using a JEOL

2010 TEM operated at an accelerating voltage of 200 keV at the University of New Mexico.

Figure 1 shows typical TEM images and corresponding electron diffraction (ED) patterns of carbon smoke particles produced under He and/or CO gas: (a) He 200 Torr, (b) He 150 and CO 50 Torr, (c) He 100 and CO 100 Torr, and (d) CO 200 Torr, respectively. The carbon particles in Fig. 1(a) are 50-100 nm in diameter, dendritic in shape, have smooth surfaces and cluster in the gas phase. The character of these carbon particles is similar to those of commonly produced amorphous carbon particles in inert gas.⁶ A typical TEM image and corresponding ED pattern of carbon particles produced in a gas mixture of He 150 Torr and CO 50 Torr are shown in Fig. 1(b). Although the particles' size and shape are similar to the carbon particles produced under He 200 Torr, the surface has become rough. The roughness of the particle surface could be caused by the CO gas. Solid carbon and CO₂ gas are produced from the catalytic decomposition of CO gas by the Boudouard reaction. Recently, the Boudouard reaction has been carried out in the production of carbon nanotubes using Mg, Ni, Fe, Co and Mo as catalytic metals.⁷⁻¹⁰ Figure 2(b) shows the high-resolution TEM (HRTEM) image of the surface of a carbon particle in Fig. 1(b). Many depositions, which appear to be short nanotubes, are visible on an amorphous particle in contrast to the surface of a carbon particle produced in He 200 Torr, shown in Fig. 2(a). Therefore it can be concluded that the Boudouard reaction occurred in this catalytic metal free system and large cage carbon particles were grown.

With increasing ratio of CO gas to He gas, the surfaces of these particles become smooth, as seen in Figs. 1(c) and (d). In particular, the size and shape of the carbon particles produced in 200 Torr of CO gas are quite similar to those of carbon particles produced in 200 Torr of He gas. However the structure of the carbon component is drastically different. Figure 2(d) shows the HRTEM image of the carbon particles produced in 200 Torr of CO. The large cages, which are similar to those on the surface of a particle in Fig. 2(b), are visible and are distributed throughout the particle. Therefore, it seems that the carbon particles were predominantly produced from the decomposition of CO gas as opposed to the evaporation of the carbon rod. In the case of particles produced in 150 Torr of He and 50 Torr of CO, the large cages are visible only on the surface, i.e., the large cages are deposited on an amorphous carbon particle, as shown in Fig 2(b). On the other hand, in the case of particles produced in 100 Torr of He and 100 Torr of CO, large cages are distributed toward the inside of the particles, i.e., amorphous core-large cage mantle, as shown in Fig 2(c). In the case of particles produced in 200 Torr of CO, an amorphous core was not visible.

When the carbon rod is evaporated in an inert gas, a rising smoke from the evaporation source can be observed. The motion of the particles follows convective currents produced by the hot rod. Large carbon particles grow by coalescence as a result of collisions among the carbon atoms and/or small particles and subsequently form clusters. The coalescence efficiency among the particles depends on the surface Debye temperature of the particles.¹¹ Since the large cages are present only on the particles' surface in the case of

production in a gas mixture of He and CO, the large cages could be deposited after production of the amorphous carbon particles. Although the evaporation temperature of carbon is quite high (~ 3000 K), the sublimation temperature of fullerenes is very low (~ 650 K). Therefore, even if amorphous carbon particles formed by the evaporation of the rod and large cages by the Boudouard reaction are simultaneously produced around the carbon rod, the amorphous core-large cage mantle structure is produced due to the large difference of coalescence temperature.

The carbon particles are also produced from carbon atoms in pure CO gas when heated by a molybdenum wire, although the quantities are less. However, the large cage structure carbon particles may be produced continuously by the introduction of fresh CO gas. Moreover, the biggest advantage of our carbon particles is that they are free of catalytic metal. Industrially, one serious problem that is always encountered is the presence of catalytic metal in carbon nanotubes. These large cage carbon particles can be regarded as short-length carbon nanotubes. This result may open the way for the production of carbon nanotubes that are free of catalytic metal.

It has been reported that the hydrogen uptake efficiency becomes higher on the SWNT with larger diameter.⁵ The mean diameter of our cage is approximately 3.8 nm, which is two times larger than the 1.85 nm diameter of the SWNT produced by Liu et al., (1999).⁵ Therefore, these particles should have the ability to store large quantities of hydrogen with high efficiency.

In order to elucidate their efficiency for hydrogen storage, carbon particles were produced under a mixture of CO and CH₄ gas. Figure 3 shows the infrared spectra over the range from 2500 to 3300 cm⁻¹ of the carbon particles produced in this gas mixture; spectrum (a) is from particles produced in 198 Torr of CO and 2 Torr of CH₄ (i.e., 1% CH₄) and spectrum (b) is from carbon particles produced in 190 Torr of CO and 10 Torr of CH₄ (i.e., 5% CH₄). The two spectra have three characteristic absorption peaks centered at ~2955, ~2925 and ~2855 cm⁻¹, which correspond to the CH₃ asymmetric stretch, CH₂ asymmetric stretch and CH₂ symmetric stretch, respectively. The mass absorption coefficients κ (cm²/g) at ~2955, ~2925 and ~2855 cm⁻¹ in spectra (a) and (b) are approximately 300, 2050 and 1150, and 600, 3350 and 1950 cm²/g, respectively. The integrated absorption strength for these samples at ~2925 cm⁻¹ is 22.7 and 42.7 cm²/g. The absorption coefficients of the C-H stretching band have been summarized by Furton et al. (1999)¹¹ using the data of Duley et al. (1998)¹². The number of C-H bonds in the carbon smoke particles can be estimated from the absorption coefficients. The absorption coefficient of the C-H stretch at 2925 cm⁻¹ is 0.44×10⁻²¹ cm² per bond.¹² The weight percent of hydrogen in these carbon particles is therefore 8.6 and 16.2 wt% for smokes produced in 1 and 5% methane, respectively. Although production of carbon particles in a pure methane gas was also carried out, it has not shown a high uptake efficiency for hydrogen. Since methane gas is decomposed by heat and produces hydrogen gas, we believe that the carbon particles adsorbed hydrogen, i.e., they did not take up methane gas. This value is 2.5 times

higher than the proposed goal for vehicular hydrogen storage set by the Department of Energy in the USA. Therefore, we believe that carbon particles produced in CO gas are a plausible candidate for use as hydrogen storage media.

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Figure captions

Figure 1. Typical TEM images and the corresponding ED patterns of carbon particles produced in (a) He 200 Torr, (b) He 150 and CO 50 Torr, (c) He 100 and CO 100 Torr, and (d) CO 200 Torr.

Figure 2. HRTEM image of carbon particles produced in (a) He 200 Torr, (b) He 150 and CO 50 Torr, (c) He 100 and CO 100 Torr, and (d) CO 200 Torr.

Figure 3. Infrared spectra ranging from 2500 to 3300 cm^{-1} of carbon particles produced in a gas mixture of CO and CH_4 , (a) 198 and 2 Torr and (b) 190 and 10 Torr, respectively. The center of these absorption peaks is at 2954, 2922 and 2851 cm^{-1} in spectrum (a) and 2957, 2924 and 2853 cm^{-1} in spectrum (b).

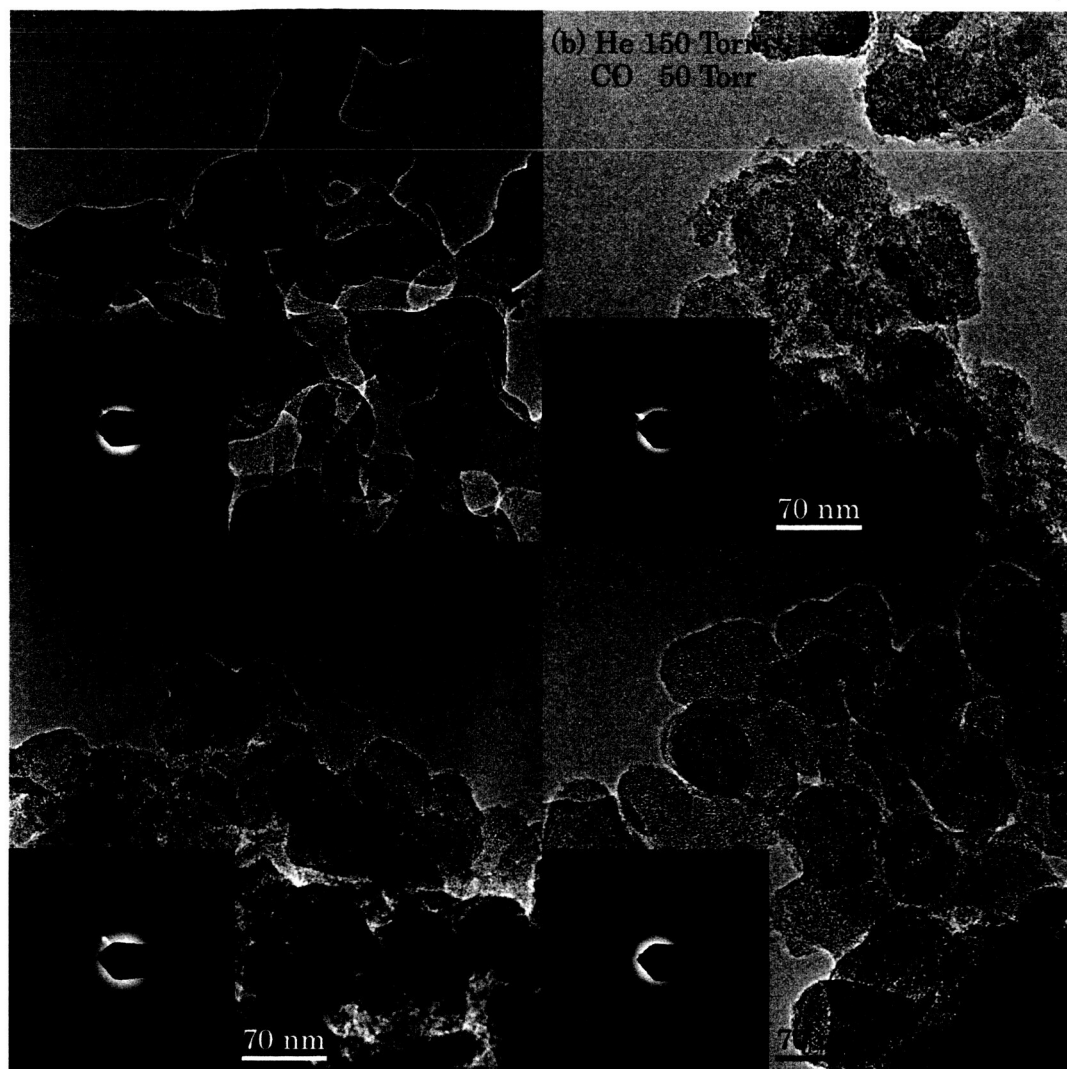


Fig. 1

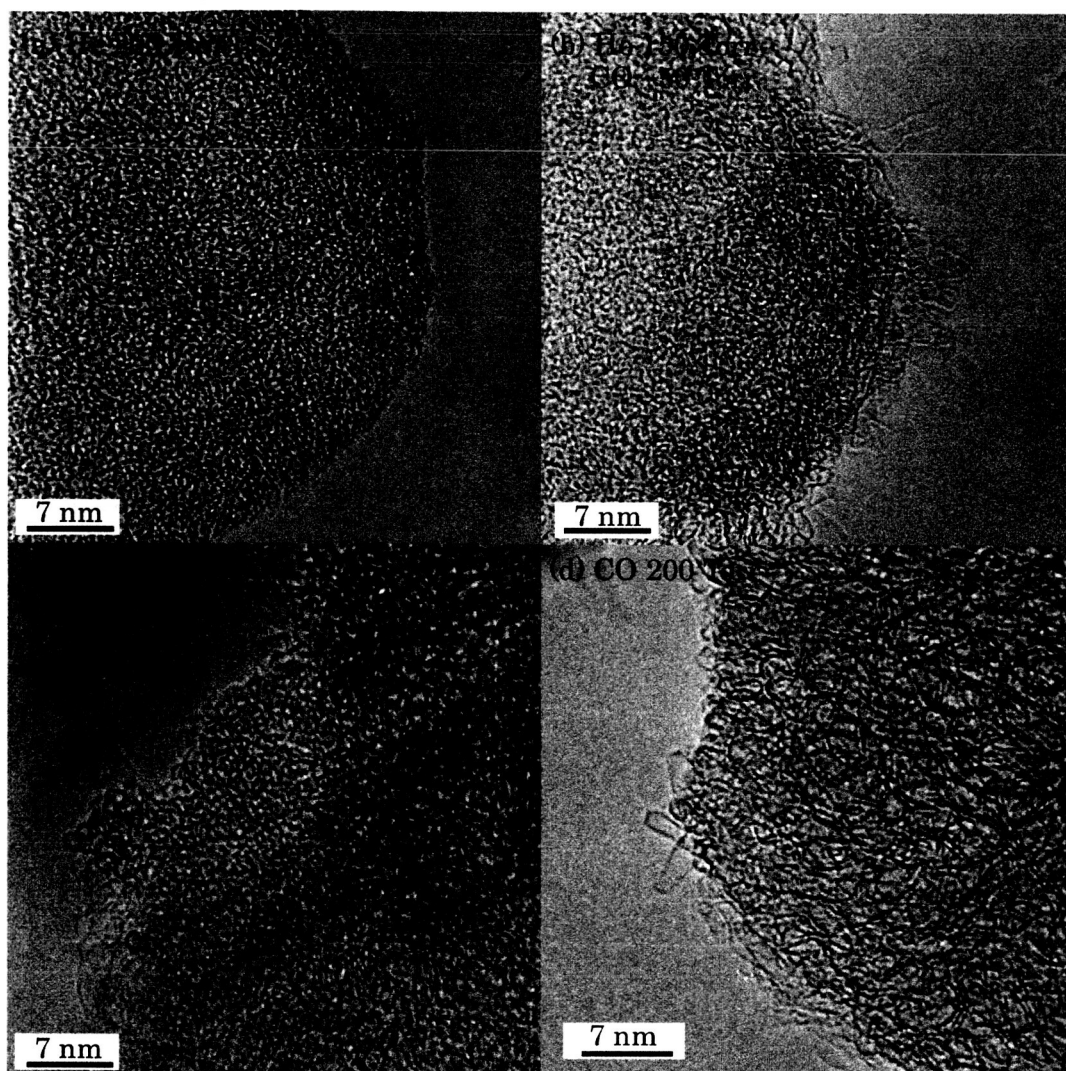


Fig. 2

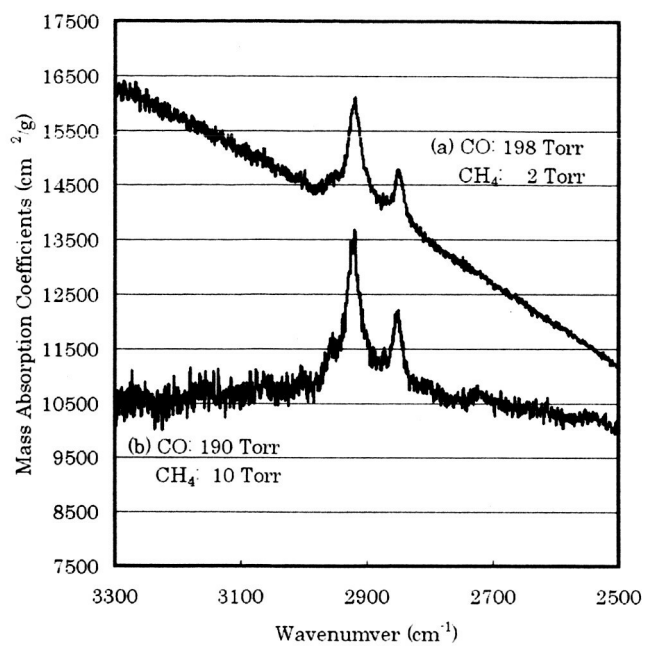


Fig. 3